High pressure polymerization of α-methylstyrene

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HIGH PRESSURE POLYMERIZATION OF α-METHYLSTYRENE

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The pressure effect on the kinetics of α-methylstyrene polymerization up to 5,000 kg/cm^2 and at various temperatures has been investigated. This polymerization system is characterized by the ceiling temperature, above which the formation of high polymer will not occur. The ratio of the rate constant of the propagation to that of the depropagation and the differences of activation parameters between them were calculated and discussed from the rate and thermodynamic equation derived by using the polymerization scheme with an accompanying depolymerization.

The molecular weight of the polymer increased with pressure and the polymerization mechanism strongly depends on the nature of solvent.

Introduction

α-Methylstyrene is readily polymerized by ionic catalysts at low temperatures. Okamura *et al.*[1] reported that the molecular weight of α-methylstyrene polymer catalyzed by boron trifluoride-diethyl ether complex at -78°C are found to range from 350,000 to 1,000,000. McCormick[2] recognized that the polymerization of this monomer in tetrahydrofuran do not occur above 61°C using sodium naphthalene complex as the initiator and calculated $\Delta H = -6.96$ kcal/mole and $\Delta S = -24.8$ cal/deg·mole. The polymerization of α-methylstyrene catalyzed by trichloroacetic acid in ethylene dichloride at 20°C was carried out by Brown and Mathieson[3].

On the other hand, it had been considered for the past several years that α-methylstyrene does not homopolymerize according to the radical mechanism[4]. Sapiro *et al.*[5] reported that polymers of α-methylstyrene are not obtained under atmospheric pressure but obtained under high pressure, at temperatures up to 125°C. However, Lowry *et al.*[6] found that α-methylstyrene was polymerized by the radical initiator under atmospheric pressure at 15°C for 5 days.

Addition polymerization reactions are the aggregation processes which are characterized by a fairly well-defined temperature, known as the ceiling temperature T_c, above which the formation of high polymer will not occur. This thermodynamic effect has been extensively investigated at ordinary

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pressure and the results are reviewed by Dainton and Ivin [7]. Kilroe and Weale [8] investigated that α-methylstyrene was allowed to react for 4 hours at various temperatures and at several pressures between 2,200atm and 6,480atm. They recognized that at each pressure the yield of polymer first increases with rising temperature and then falls steeply to zero as T_c is approached and the relation between $\log T_c$ and pressure is linear. Investigation of the ceiling temperature phenomena involves the determination of monomer-polymer equilibria as a function of temperature and pressure. The effect of pressure on the equilibria between monomer and its polymer were recognized in the case of the polymerization of chloral[9] and *n*-butylaldehyde[10].

Moreover, unordinary polymerization methods of α-methystyrene, high temperature catalyzed polymerization at 290~350°C [11] and radiation induced solid phase polymerization [12] are reported.

Although the literature contains several references to the polymerization of α-methylstyrene by radical mechanism, the investigation of this polymerization has not been extended beyond the relation of polymerization possibility and ceiling temperature. The present investigation was undertaken to determine the kinetic parameters and the effects of pressure and temperature on conversion, molecular weight and polymer-monomer equilibrium.

Experimental

Materials

α-Methylstyrene, initially commercially purified materials, was washed with 5% sodium hydoxide solution and pure water, dried with calcium chloride overnight, distilled twice under reduced nitrogen pressure and stored in a freezing box with nitrogen gas.

Azobisisobutironitrile used as the initiator was recrystallized twice from ethanol solution and dried *in vacuo*.

Tetrahydrofuran was dried with potassium hydroxide, and distilled twice.

n-Butylacetate, benzene, cyclohexanone and pyridine were distilled with the commercial reagents.

Polymerization procedure

The polymerization reaction was carried out in 10ml capacity glass sliding tube immersed in a high pressure autoclave. The polymer mixture thus obtained was precipitated into a large amount of methanol as a precipitant, dried completely *in vacuo* at room temperature, and its polymerization yield was determined. The polymer for viscosity measurement was reprecipitated by the methanol-

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tetrahydrofuran system.

Since the polymerization reaction scarcely occurred below 2,000 kg/cm^2 within our experimental conditions and the kinetic analysis was difficult, all experiments were done above 2,000 kg/cm^2 pressure.

Kinetic and thermodynamic equation

As the polymerization of α-methylstyrene follows the depropagation step as well as the ordinary step, the reaction is represented schematically as follows,

$$\left.\begin{aligned} \mathrm{I} &\longrightarrow 2\mathrm{R}\cdot \\ \mathrm{R}\cdot + \mathrm{M} &\longrightarrow \mathrm{M}\cdot \end{aligned}\right\} \quad R_i$$

$$\mathrm{M}_n\cdot + \mathrm{M} \longrightarrow \mathrm{M}_{n+1}\cdot \quad k_p$$

$$\mathrm{M}_{n+1}\cdot \longrightarrow \mathrm{M}_n\cdot + \mathrm{M} \quad k_d$$

$$\mathrm{M}_m\cdot + \mathrm{M}_n\cdot \longrightarrow \text{polymer} \quad k_t$$

where I is an initiator, R· a primary radical, M a molecule of monomer, $\mathrm{M}_n\cdot$ a polymer radical with n monomer units in the chain, R_i the rate of initiation, k_p the propagation rate constant, k_d the depropagation rate constant and k_t the termination rate constant. Application of the stationary state theory would lead to a rate equation,

$$R_p=\left(\frac{R_i}{k_t}\right)^{1/2}k_p[\mathrm{M}]-\left(\frac{R_i}{k_t}\right)^{1/2}k_d\,, \tag{1}$$

where [M] is the monomer concentration.

It is reasonable to expect that the pressure contributes to accelerate k_p and retard k_d, as this result α-methylstyrene is enable to convert into a polymer of high molecular weight.

Ignoring the chain transfer reaction, the degree of polymerzation will be given by

$$\bar{P}=\frac{k_p}{(R_i\cdot k_t)^{1/2}}[\mathrm{M}]-\frac{k_d}{(R_i\cdot k_t)^{1/2}}\,. \tag{2}$$

Dainton and Ivin[7] introduced the concept of ceiling temperature T_c in the following equation,

$$T_c=\frac{\Delta H}{\Delta S+R\ln[\mathrm{M}]}\,. \tag{3}$$

where ΔH is the heat of polymerization, ΔS the corresponding entropy and R the gas constant. Equation (3) defines a ceiling temperature at which the propagation and depropagation of the growing chains in an addition polymerization occur at equal rates.

Accordingly, the relation between the reaction temperature T and the equilibrium monomer concentration [m] is given as follows,

$$T=\frac{\Delta H}{\Delta S+R\ln[\mathrm{m}]}\,. \tag{4}$$

$$\frac{1}{T}=\left(\frac{R}{\Delta H}\right)\ln[\mathrm{m}]+\frac{\Delta S}{\Delta H}\,. \tag{5}$$

Results and discussions

Rate constant

The overall polymerization rate was calculated from the slope of time-conversion curve below 5% because the plot of the conversion against the polymerization time was found to be linear at low conversion.

The relations between monomer concentrations and the polymerization rate at different pressures and temperatures are shown in Figs. 1 and 2. Unless otherwise stated, all polymerizations were carried out in tetrahydrofuran as the solvent. The polymerization rate showed a linear relation with the monomer concentrations as expected from equation (1), and the rate increased with pressure. The intersection on the abscissa defines an equilibrium monomer concentration at which the propagation

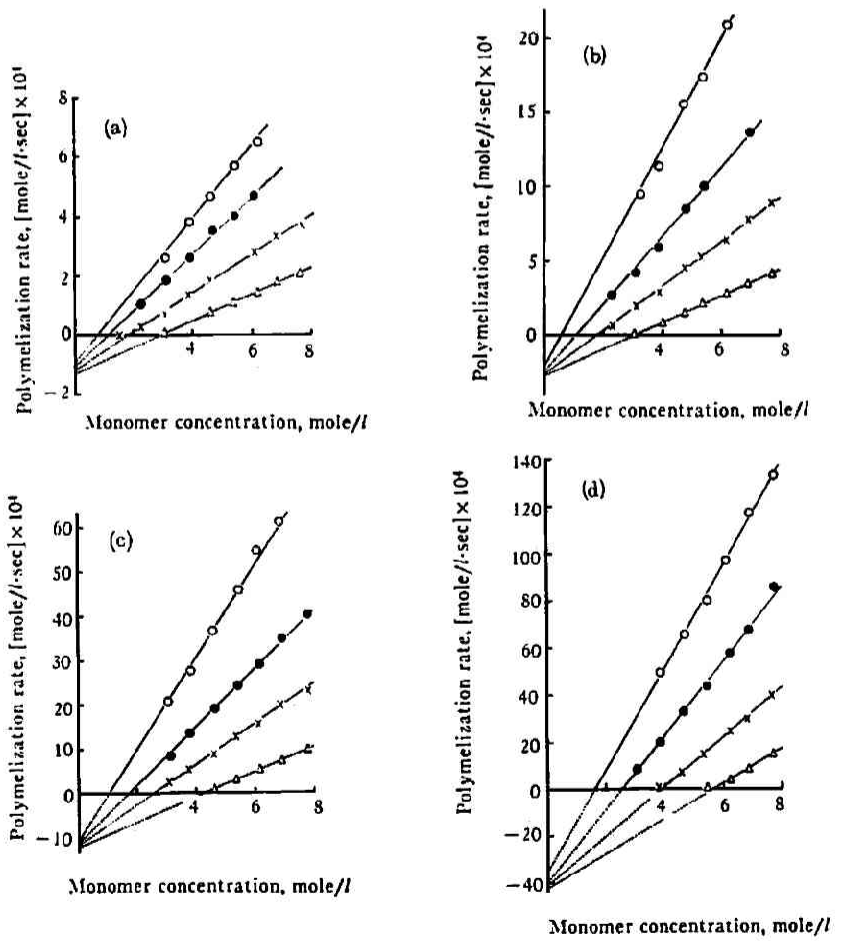

Fig. 1 Variation of polymerization rate with monomer concentration and pressure
—△— 2,000 kg/cm², —×— 3,000 kg/cm², —●— 4,000 kg/cm², —○— 5,000 kg/cm²
(a): 50°C, (b): 60°C, (c): 70°C, (d): 80°C

and depropagation of the growing chains in the polymerization occur at an equal rate. These values decreased with pressure. The first term of equation (1), $(R_i/k_t)^{1/2}k_p$, can be calculated from the slope of this line and the second term, $(R_i/k_t)^{1/2}\cdot k_d$, can be estimated from the intersection on the ordinate. The results are summarized in Table 1. It was found that the increase in pressure resulted in a large k_p/k_d, but the value of k_p/k_d decreased with temperature except for the experiment at 50°C.

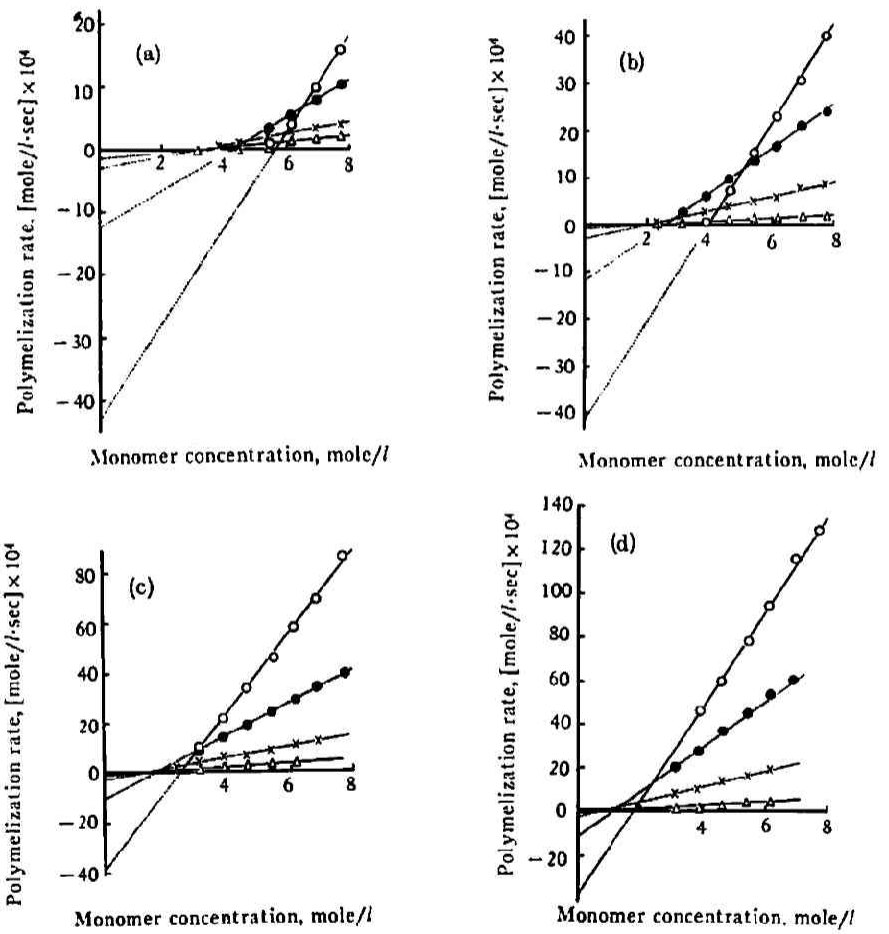

Fig. 2 Variation of polymerization rate with monomer concentration and temperature
—△— 50°C, —×— 60°C, —●— 70°C, —○— 80°C
(a): 2,000 kg/cm², (b): 3,000 kg/cm², (c): 4,000 kg/cm², (d): 5,000 kg/cm²

Polymerization heat and entropy

The values of $1/T$ were plotted against ln[m] as shown in Fig. 3. The plots are linear except in the case at 50°C. The deviation from this straight line at 50°C increased with pressure. While the the relation of the polymerization rate to the monomer concentration at 50°C showed good linearity and the break-down of the glass testing tube filled with high concentrated monomer was recognized at 50°C.

Table 1 Rate constant and equilibrium monomer concentration

Temperature (°C)	Pressure (kg/cm²)	$\left(\frac{R_i}{k_t}\right)^{\frac{1}{2}}k_p$ (sec⁻¹)	$\left(\frac{R_i}{k_t}\right)^{\frac{1}{2}}k_d$ (mole/l·sec)	$\frac{k_p}{k_d}$ (1/mole)	Equilibrium monomer concentration (mole/l)
50	2,000	0.436	1.3	0.335	2.99
	3,000	0.688	1.2	0.573	1.75
	4,000	0.953	1.1	0.866	1.15
	5,000	1.233	1.0	1.233	0.81
60	2,000	0,926	2.8	0.331	3.02
	3,000	1.545	2.7	0.572	1.85
	4,000	2.417	2.6	0.930	1.08
	5,000	3.759	2.4	1.566	0.64
70	2,000	2.940	12.2	0.241	4.15
	3,000	4.708	12.1	0.389	2.58
	4,000	6.970	11.9	0.586	1.71
	5,000	10.500	11.6	0.905	1.11
80	2,000	7.652	43.0	0.178	5.62
	3,000	10.620	42.0	0.253	3.95
	4,000	15.860	40.0	0.397	2.52
	5,000	22.030	38.0	0.580	1.72

These facts suggest that the above deviation may be caused by the freezing of the monomer under high pressures. Thus, freezing of α-methylstyrene under pressure was found also by Weale *et al.*[13].

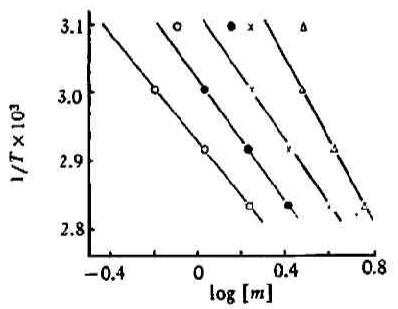

Fig. 3 Temperature dependence of equilibrium concentration of α-methylstyrene
—△— 2,000 kg/cm²
—×— 3,000 kg/cm²
—●— 4,000 kg/cm²
—○— 5,000 kg/cm²

Accordingly, the net amount of monomer presented in the reaction region would be lower. Assuming that the frozen monomer does not react, the freezing amount of the monomer was calculated from the deviation from the straight line and listed in Table 2.

The freezing amount of α-methylstyrene increased with pressure. As shown in Fig. 4, the van't Hoff plots corrected by the freezing amount are reasonable.

The values of ΔH and ΔS obtained from Fig. 3 are given in Table 3. The effect of pressure on the entropy term was more strikingly marked than on the energy term.

Table 2 Effect of pressure on the freezing of α-methylstyrene

Pressure (kg/cm²)	Freezing amount of α-methylstyrne (%)
2,000	28
3,000	34
4,000	41
5,000	53

Table 3 Polymerization heat and entropy

Pressure (kg/cm²)	ΔH (kcal/mole)	ΔS (cal/mole·deg)
1 (extrapolating)	−4.00	−16.4
2,000	−7.09	−23.4
3,000	−9.20	−28.7
4,000	−9.98	−30.1
5,000	−11.58	−33.8

Since the relations of ΔH and ΔS to pressure are almost linear as shown in Fig. 5, the enthalpy and entropy at atmospheric pressure, $\Delta H = -4.0$ kcal/mole, $\Delta S = -16.4$ cal/deg·mole, can be estimated by the extrapolation. These values are somewhat larger than the values obtained by McCormick[2], $\Delta H = -6.96$ kcal/mole, $\Delta S = -24.8$ cal/deg·mole.

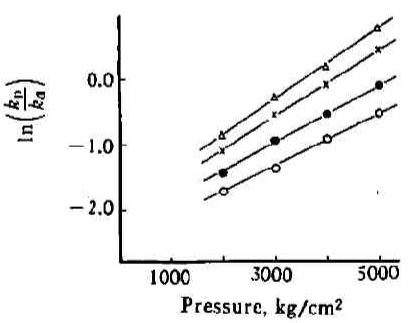

Fig. 4 van't Hoff plots of rate constant
—△— 50°C, —×— 60°C
—●— 70°C, —○— 80°C

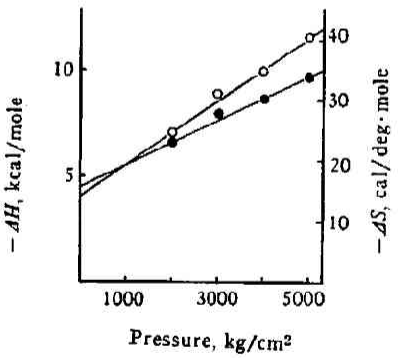

Fig. 5 Pressure dependence of the polymerization heat and entropy
—○— polymerization heat
—●— polymerization entropy

Activation volume

The activation volume was calculated from the van't Hoff plots as shown in Fig. 4. The rate data at 50°C were corrected by the freezing amount of the monomer. The results of calculations are summarized in Table 4.

Table 4 Activation volume

Temperature (°C)	$\Delta V^{\neq}$ (cm³/mole)
50	−14.5
60	−13.8
70	−11.8
80	−10.7

These values refer to standard for 2,000 kg/cm² pressure because the polymerization does not take place under atmospheric pressure. However, the differences of the activation volume between propagation and depropagation were negative and decreased with temperature. The result indicates that the volume of transition state of the propagation reaction is considerably larger than the volume of transition state of the depropagation reaction, *i.e.* the structure of the two activated complexes are notably different.

Molecular weight

The molecular weights of the polymer obtained were not measured directly, but the intrinsic viscosity $[\eta]$ was determined as an approximate indication, whose relation to the monomer concentration, temperature and pressure are shown in Figs. 6 and 7. The values of $[\eta]$ increased with the monomer concentrations as expected in equation (2), the pressure and temperature dependency of $[\eta]$ showed that the molecular weight of the polymer increased with pressure and temperature.

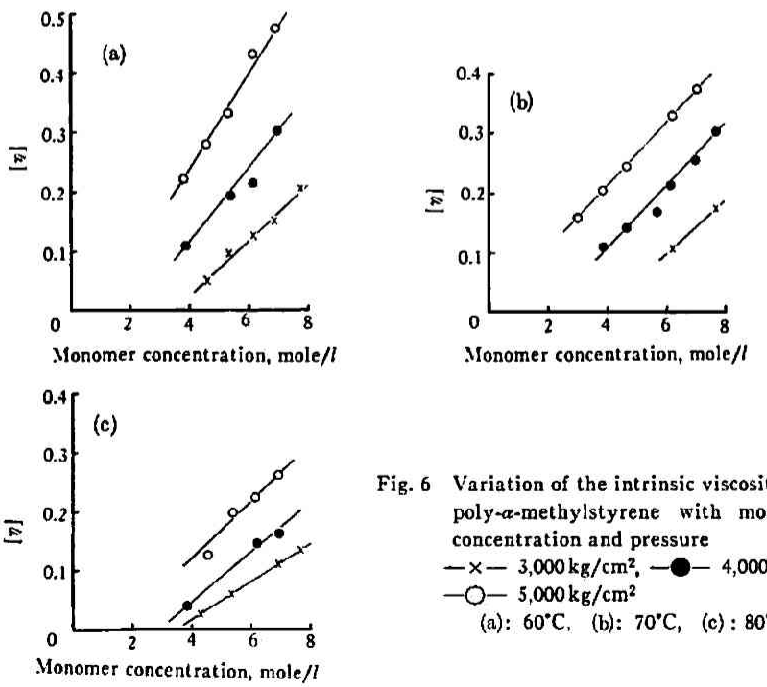

Fig. 6 Variation of the intrinsic viscosities of poly-α-methylstyrene with monomer concentration and pressure
—×— 3,000 kg/cm², —●— 4,000 kg/cm²
—○— 5,000 kg/cm²
(a): 60°C, (b): 70°C, (c): 80°C

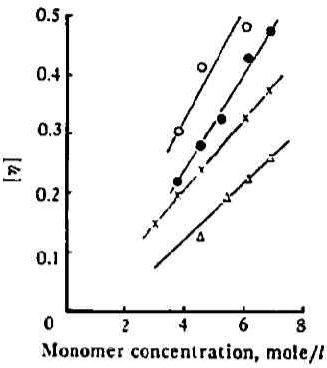

Fig. 7 Variation of the intrinsic viscosities of poly-α-methylstyrene with monomer concentration and temperature at 5,000 kg/cm²
—△— 50°C, —×— 60°C
—●— 70°C, —○— 80°C

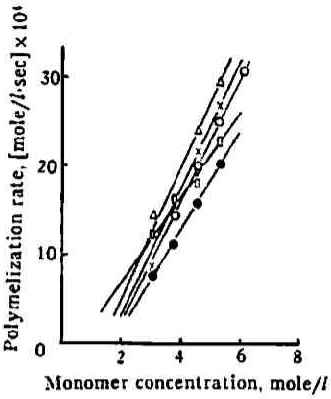

Fig. 8 Effect of solvent on the polymerization rate
—□— benzene
—△— cyclohexanone
—○— tetrahydrofuran
—●— *n*-butylacetate
—×— pyridine

Effect of solvent

The effect of the monomer concentrations on the over-all polymerization rates in several organic solvents are shown in Fig. 8. All the experiments were done at 70°C and 4,000 kg/cm² pressure. The values of k_p/k_d calculated by the same method and the dielectric constant of the solvent are listed in Table 5. The values of k_p/k_d were affected by the dielectric constant of the solvent. These facts suggest that the polymerization mechanism of α-methylstyrene strongly depends on the nature of solvent.

Table 5 Dielectric constant of the solvent and rate constant

Solvent	Dielectric constant	k_p/k_d
Benzene	2.28	1.610
n-Butylacetate	5.01	0.568
Tetrahydrofuran	8.20	0.586
Pyridine	12.30	0.609
Cyclohexanone	18.30	0.720

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